AD/A-004 405

REACTIONS OF THE LOW-TEMPERATURE TRANSFORMATION OF AMMONIUM PERCHLORATE

V. A. Koroban, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

27 November 1974

HDH-004405

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Foreign Technology Division	UNCLASSIFIED
Air Force Systems Command	2b. GROUP
U. S. Air Force	

3. REPORT TITLE

REACTIONS OF THE LOW-TEMPERATURE TRANSFORMATION OF
AMMONIUM PERCHLORATE

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Translation

5. AUTHOR(S) (First name, middle initial, last name)

V. A. Koroban, B. S. Svetlov, and V. M. Chugunkin

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
1972	13	4

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	FTD-MT-24-2022-74
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Foreign Technology Division
	Wright-Patterson AFB, Ohio

13. ABSTRACT

20

DD FORM 1473
1 NOV 65

i

EDITED MACHINE TRANSLATION

REACTIONS OF THE LOW-TEMPERATURE TRANSFORMATION
OF AMMONIUM PERCHLORATE

By: V. A. Koroban, B. S. Svetlov, and
    V. M. Chugunkin

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
A a	*A a*	A, a	P p	*P p*	R, r
Б б	*Б б*	B, b	C c	*C c*	S, s
В в	*В в*	V, v	Т т	*T m*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	X x	*X x*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	ь ь	*ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.
The use of diacritical marks is preferred, but such marks
may be omitted when expediency dictates.

* * * * * * * * *

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc.
merged into this translation were extracted
from the best quality copy available.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	$\sech^{-1}$
arc csch	$\csch^{-1}$

Russian	English
rot	curl
lg	log

GREEK ALPHABET

Alpha	A	α	✱	Nu	N	ν	
Beta	B	β		Xi	Ξ	ξ	
Gamma	Γ	γ		Omicron	O	o	
Delta	Δ	δ		Pi	Π	π	
Epsilon	E	ε	ϵ	Rho	P	ρ	ϱ
Zeta	Z	ζ		Sigma	Σ	σ	ς
Eta	H	η		Tau	T	τ	
Theta	Θ	θ	ϑ	Upsilon	T	υ	
Iota	I	ι		Phi	Φ	φ	ϕ
Kappa	K	ϰ	κ	Chi	X	χ	
Lambda	Λ	λ		Psi	Ψ	ψ	
Mu	M	μ		Omega	Ω	ω	

REACTIONS OF THE LOW-TEMPERATURE TRANSFORMATION OF AMMONIUM PERCHLORATE

V. A. Koroban, B. S. Svetlov, and V. M. Chugunkin

Moscow

Recently a sufficient quantity of facts have been obtained which attest to the fact that the low-temperature decomposition of ammonium perchlorate (APC) [ПХА] begins from the stage of the dissociation of the salt to ammonia and perchloric acid. However, in respect to the further development of the process, until now there is no unified opinion. It is logical to assume that following dissociation the decomposition of perchloric acid occurs. Its breakdown in vapors will not ensure the initial velocity of decomposition of APC even with the full dissociation of the salt. The rate of the decomposition of the vapors of 100% perchloric acid at a pressure of 20 mm Hg in the presence of APC (m/V=0.8 g/cm^3) at 150°C proved to be 4 orders higher than the rate calculated for vapors according to Levi [1], but 6 orders lower than that which should correspond to the initial rate of decomposition of APC at the equilibrium pressure of acid. The higher decomposition rate of $HClO_4$ in the presence of APC can be explained by the heterogenic nature of the process. In order to obtain a concept about the adsorption of acid, we carried out experiments on the study of absorption of 100% $HClO_4$ by ammonium perchlorate.

The perchloric acid, obtained from the reaction of dihydrate with concentrated H_2SO_4, was refrozen into a vessel of known volume, equipped with a glass compensation manometer. The vessel with $HClO_4$ was separated from the vessel with APC by a fine glass partition. The APC was thoroughly evacuated in 2-3 h at 100°C. After measurement of the quantity of $HClO_4$ based on the pressure of its vapors at 80°C and a ratio $p/p_s = 0.05$ the partition was broken open with a striker and equilibrium pressures of $HClO_4$ measured in the presence of APC from 50 to 120°C with an interval of 5-10°. From Fig. 1, where the results of the experiment in coordinates $\lg \theta/p - 1/T°K$ are represented (θ - absorption of $HClO_4$ in cm^3/g), it is evident that with small degrees of absorption of heat the adsorption is significantly higher (24 kcal/mole) than the heat of condensation of $HClO_4$ (10 kcal/mole). From the findings it follows that the filling of the monomolecular layer at a pressure of 20 mm Hg is finished only at 90°C. The calculation shows that under the conditions of the experiment on the decomposition of the vapors of acid in the presence of APC the degree of filling of the surface of the salt should not exceed 10%. Hence the comparatively low decomposition rate of $HClO_4$ in this case, referred to its total quantity, cannot be explained by the saturation of the surface.
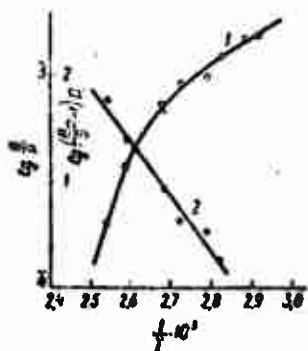

Figure 1. Dependence of the absorption of perchloric acid by ammonium perchlorate on temperature (1) and semilogarithmic anamorphism in coordinates of the Langmuir equation (2).

The discovered nonconformity between the decomposition rate of APC and the perchloric acid adsorbed on it indicates the insignificant role of the outer surface. Further, since the decomposition rate of APC under parafin in the presence of excess

$CaCO_3$ and with the pulverizing of the salt is changed weakly, then the portion of perchloric acid on the outer surface is obviously low, and the decomposition products, abandoning the condensed phase, do not participate in the development of the process. The experiments showed that the decomposition of APC in the presence of liquid 72% perchloric acid, obeying the law of volumetric increase in the nucleus ($V=Kt^3$), has K only 2-3 times higher than during decay of APC without an additive. The rate of decomposition of samples, having perchloric acid only within the crystals, is changed from the content of the latter on the saturating curve with the approximate equation $dv/dt = A[H^+]^p$, here the rate reached a constant value at a concentration of $HClO_4$ of 10^{-3} mole %. This could be observed, if the decomposition of perchloric acid begins in a comparatively small number of potential centers, the number of which is not changed substantially with the introduction of acid or its formation during decomposition. According to known data [2], the centers of the reaction appear only at a depth of ~3 μ in places with an increased dislocation density, and the development of the process of decomposition of APC is accompanied by the multiplication of dislocations near the growing zone of decomposition [3]. Furthermore, according to Boldyrev the decomposition is accelerated by cation vacancies [4]. It is possible to assume that in this case perchloric acid appears during the interaction of cation vacancies with protons, and during decay - as a result of the removal of ammonia from the NH_4^+ cation. The formation of perchloric acid in this form and its further breakdown should be facilitated near dislocations. On the presence of perchloric acid in the reaction vessel or the crystals of APC the activation energy of the initial decay rate of APC depended weakly and was found within the limits of 27-31 kcal/mole, being retained also at the subsequent stages of decomposition when significant quantities of $HClO_4$ were accumulated. These facts indicate that the basic contribution to the activation energy of the decomposition of APC is made by the activation energy of the decomposition of perchloric acia. The

concentration of $HClO_4$ in the condensed phase during the dissociation of APC should depend on temperature weakly, since the heat of adsorption of $HClO_4$ by the salt is 24 kcal/mole.

In order to finally solve the question concerning the role of perchloric acid during the decomposition of APC it is necessary to verify that with a reasonable content of it, it can be decomposed at the same rate as APC in the beginning of decomposition. The expected values of the decomposition rates of $HClO_4$ in the crystals of APC, calculated in terms of the initial rate of breakdown of the sample containing an admixture of $HClO_4$ and on the auto-catalytic rate constant of decomposition in comparison with the rates of decomposition of perchloric acid at 170° are given in Table 1. It is evident that the rate of decomposition of perchloric acid in the adsorbed state approaches the rate of its decomposition in crystals.

Table 1. Comparison of the decomposition rates of perchloric acid at 170°C.

State of $HClO_4$	ω, 1/s	E, kcal/mole
Vapors	$2 \cdot 10^{-9}$	45
Liquid dihydrate	10^{-7}	44
Adsorbed on APC	$10^{-3}-10^{-2}$	–
In APC, calculated from the initial decomposition rate	$10^{-3}-10^{-4}$	27-30
In APC, calculated from the constant on the stage of acceleration	$10^{-3}-10^{-2}$	27-30

During decomposition of $HClO_4$ intermediate products are formed with such a high reactivity that it is possible to expect their

rapid interaction with APC. As a model for a study of this stage we have selected systems which consist of APC and ClO_2. The experiments showed that the dry oxides of chlorine at low temperatures virtually do not react with APC, but at increased (above 100° C) are decomposed rapidly with formation only of a small amount of nitrogen-bearing gases. The analogous result is obtained in the experiment on APC, to which 5% dihydrate of perchloric acid is added (Fig. 2, curve 1; Table 2). In the presence of H_2O (5%) even at 70°C a rapid pressure drop occurred (curve 2), and gaseous products consisted mainly of N_2O and N_2. The oxides of chlorine were reduced in this case to HCl. In the presence of 57% acid (curve 3) ClO_2 interacted with APC, being reduced to Cl_2. The composition of products in this case coincided with the composition of the decomposition products of APC; virtually only oxygen was absent. With ammonia ClO_2 reacted at room temperature instantly with the formation solely of nitrogen in the gases.

Figure 2. Change in the quantity of gases during the reaction of ClO_2 in the presence of ammonium perchlorate and additives: 1 - 5% perchloric acid (dihydrate); 2 - 5% water; 3 - 5% perchloric acid (57%).
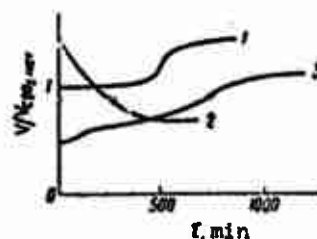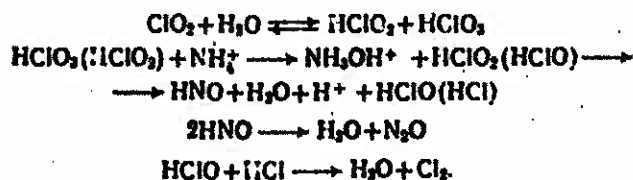

Table 2. Composition of the end products of transformation of ClO_2 with ammonium perchlorate.

Additive	Fraction of gases in end products, %			
	Cl_2	O_2	N_2	N_2O
H_2O (5%)	-	3.6	9.5	23
57% $HClO_4$ (5%)	21	1.3	8	13
72% $HClO_4$ (5%)	28	31	0.7	0.3
Decomposition of NH_4ClO_4	12	13	6.3	8.7

The observed effect of moisture and acidity of the medium on
the reaction rate and the composition of the end products of the
oxidation of APC by chlorine dioxide can be explained by the fact
that the oxidizing agents are chloro-oxyacids, the stability of
which in an acid medium drops from $HClO_3$ to $HClO$, and the concentra-
tion of free NH_3 does not play a significant role. The oxidation
of the NH_4^+ ion flows probably according to the reactions

$$ClO_2 + H_2O \rightleftharpoons HClO_2 + HClO_3$$
$$HClO_3(HClO_2) + NH_4^+ \longrightarrow NH_2OH^+ + HClO_2(HClO) \longrightarrow$$
$$\longrightarrow HNO + H_2O + H^+ + HClO(HCl)$$
$$2HNO \longrightarrow H_2O + N_2O$$
$$HClO + HCl \longrightarrow H_2O + Cl_2.$$

The liberation of nitrogen, apparently, occurs during the
breakdown of the ammonium salts which are generated during the
exchange interaction of the lowest chloro-oxyacids with APC.
The results of the experiments on concentrated perchloric acid are
found in accordance with the findings on the oxidation of APC. At
temperatures below 100°C and pressures of vapors 2-5 times lower
than the pressure of the saturated vapor the acid is decomposed
without participating in an interaction with APC. By taking into
account the low volatility of dihydrate, the dependence of the rate
of oxidation of APC and decomposition of $HClO_4$ on concentration,
it is possible to expect that in reaction nuclei the concentration
of $HClO_4$ does not exceed 72%. This acid, obviously, conditions
the diffusion of NH_3 from the adjacent dislocations. Oxidation
processes flow most intensively in reaction nuclei; however, the
decomposition of perchloric acid in them also occurs quite rapidly.
The comparison of the decomposition rates of APC with the sample
which contain ClO_3^- ions, where the reaction nuclei appear very
rapidly, shows that the decomposition rate of the substance, and
consequently also $HClO_4$, in them is even somewhat higher than the
rate of transformation of $HClO_4$, in a crystal. Thus the decomposi-
tion of APC is caused by the decomposition of $HClO_4$ in the
lattice of the salt, which leads to the appearance of reaction
nuclei which contain perchloric acid and products of its

decomposition. In these nuclei the oxidation of APC occurs and
the formation of an additional amount of $HClO_4$. This acid causes
the formation of new reaction nuclei on the adjacent defects.

BIBLIOGRAPHY

1. J. B. Levy. J. Phys. Chem., 1962, 66, p. 1092.
2. А. В. Раевский, Г. Б. Манелис. Докл. АН СССР, 1963, 151, стр. 886.
3. А. В. Раевский, Г. Б. Манелис, В. В. Болдырев, Л. А. Вотинова.
Докл. АН СССР, 1965, 160, стр. 1156.
4. V. V. Boldyrev, V. V. Alexandrov, A. V. Boldyreva, V. I. Gritsan,
Yr Ye. Karpenko, O. P. Korobeinitchev, V. N. Panfilov, E. F. Khairet-
dinov. Combustion and Flame, 1970, 15, p. 71.